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An Improved Ion Guide for External Ion Injection  
in Glow Discharge -Fourier Transform Ion Cyclotron  
Resonance (GD-FTICR) Mass Spectrometry

by

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To improve the existing ion transport optics of our glow discharge-Fourier transform ion cyclotron resonance (GD-FTICR) mass spectrometer, we have simulated several ion trajectories between the glow discharge source region and the ICR analyzer cell. These calculations suggested that a number of simple improvements, including the use of an ion flight tube and an electrically isolated conductance limit, would increase the efficiency of ion transfer through the fringing fields of the FTICR superconducting magnet and into the ICR analyzer cell. Ion beam intensity was monitored before and after implementing these improvements as a function of the distance between the glow discharge source and the analyzer cell. A twenty-fold improvement in the transport efficiency, as well as a significant enhancement in detected FTICR signals, was observed.

**92-14663**



## **INTRODUCTION**

Ion generation external to the analyzer cell in Fourier transform ion cyclotron resonance (FTICR) mass spectrometers has proven to be a powerful means of obtaining mass spectral information from ionization sources that operate above the relatively low conventional pressure requirements ( $10^{-6}$  -  $10^{-8}$  Torr) necessary for high resolution and good signal-to-noise ratios. Both the dual cell approach [1], in which ion formation takes place in a higher pressure source region adjacent to a lower pressure analyzer region, and approaches in which ions are generated external to the magnetic field and then transported through several stages of differential pumping [2,3], have permitted the use of such varied sample introduction/ionization techniques as fast-atom bombardment, gas chromatography, and supersonic expansion in combination with FTICR mass analysis [4-6].

In a previous publication [7], we described how external injection of glow discharge (GD) generated ions was facilitated by a relatively simple four element electrostatic lens that accelerated and focussed ions exiting the high pressure region of the GD ion source. Other than this lens no other acceleration, focussing, or deceleration was employed. Quantitative analysis at analyte levels of 0.1% and above was demonstrated, along with mass resolution ( $m/\Delta m_n$ ) in excess of 40,000 (4 times higher than any commercial glow discharge mass spectrometer). Although the spatial distribution and energy spread of glow discharge generated ions is small [8], we believe the sensitivities demonstrated for other GDMS instruments [9,10] indicate that other factors, such as the "magnetic mirror effect" [11] or collisional scattering of ions by the relatively high gas pressures they encounter during their transport from the source, are playing a role in determining the total number of ions observed in the analyzer. Figure 1 illustrates the variation in magnetic field strength, measured by a gaussmeter, along the primary injection axis (z-axis) for the 2.0 Tesla superconducting magnet used in our FTICR-MS system. The "rear" trap plate is defined as the plate farthest from the glow discharge source. As the field is measured from the GD source (45" from the "rear" trapping plate) to the analyzer cell, an increase from 95 G to 20,000 G is observed. It is reasonable to assume that the transport of ions over this region is tenuous, and that our prior success can be attributed to the abundant population and small energy spread of ions exiting the GD source.

In this paper, we report some efforts to circumvent the effects of the magnetic field on ion transport. Preliminary results are presented for an ion flight tube/decelerator combination that transports ions through the fringing fields of the magnet with minimal loss. Also addressed are the next logical steps for further increasing sensitivity, as well as the future role of GD-FTICR in the elemental mass spectrometry community.

## **EXPERIMENTAL**

A GD-FTICR mass spectrometer that is capable of high resolution elemental mass spectrometry has been described in detail elsewhere [7]; however, several modifications implemented to improve ion transport are presented here. Figure 2 illustrates the

orientation of components in the modified instrument. One simple improvement over the previous design was addition of an electrically isolated conductance limit (CL), containing a 1.0 mm diameter orifice, to which a variable voltage could be applied. This conductance limit had previously been maintained at ground potential and used only to restrict gas flow from the source to the analyzer region. Additionally, an electrically isolated ion flight tube was fabricated from a 1.5" o.d. x 0.0625" wall 304 stainless steel tube 39" long; this tube was positioned 1.0" behind the conductance limiting orifice along the injection (z) axis. Similarly, an ion decelerator consisting of an electrically isolated ring electrode (1.0" o.d. x 0.75" i.d. x 0.1" long) and a grounded housing (1.0" o.d. x 0.75" i.d. x 3.0" long) was machined from 304 stainless steel and positioned 0.5" from the flight tube and 0.1" in front of the entrance trapping plate of the analyzer cell. This decelerator was similar in design to that reported previously by Kofel and McMahon [12]. For these studies, two stages of differential pumping were maintained by a 150 L/s turbomolecular pump at the ion source and two 300 L/s and one 700 L/s diffusion pumps at the analyzer (all three diffusion pumps were beyond the conductance limiting orifice). One initial observation was that with the flight tube in place, the pressure in the high vacuum region increased 50 fold (from  $1 \times 10^{-7}$  Torr to  $5 \times 10^{-6}$  Torr), due to lower conductance with the flight tube and its supporting system. After modifying the flight tube with a series of one hundred sixty 0.0625" diameter holes along its length, it was possible to maintain an analyzer pressure of  $1.0 \times 10^{-7}$  Torr while the glow discharge source was operating at 1.0 Torr argon pressure.

The "abnormal" [8] glow discharge used for ion formation in these studies was formed about a machined 2.0 mm diameter pin cathode positioned on the end of a direct insertion probe (DIP); this DIP permitted manipulation of the cathode to anode separation distance. The GD was operated with a constant current of 2.0 mA at 1500 V dc and at a constant pressure of 1.0 Torr argon. The cathode to anode separation distance was maintained at 8.0 mm for all of these studies.

A total ion current detection method was developed using a Faraday cup/probe built in this laboratory. The probe was constructed from a 5 kV high voltage feedthrough welded into a 0.5" o.d. x 0.0625" wall stainless steel tube whose total length was 97.5". A 0.5" diameter stainless steel Faraday cup was positioned on the end of the feedthrough, and the ion beam current was measured directly by an electrometer (Keithley Model #610C). The Faraday probe was inserted through a 0.5" diameter solids insertion probe vacuum interlock to permit manipulation along the z-axis in the vacuum chamber. The probe passed through the ICR analyzer cell (trapping plates open) and could be extended to within a few millimeters of the cell side of the conductance limit. In this manner, the ion beam intensity could be measured from the conductance limit to the analyzer cell without breaking vacuum.

When normal FTICR detection was needed, the probe was removed from the vacuum chamber, grid trapping plates reattached to the cell, and a typical pulse sequence employed; this pulse sequence usually consisted of dropping the trapping plates from +2

V to ground for a period of 0.1 - 5.0 seconds (to allow ions to be "injected" into the analyzer cell), followed by raising the plates back to +2 V for the detection phase. No ion ejection was used for any of the studies reported here. Ions with cyclotron frequencies from 10 kHz to 2.667 MHz were excited and detected with a bandwidth of 2.667 MHz. In the conventional detection scheme, fifty time domain signals of 16 k data points each were accumulated. The averaged signal was apodized by a modified Blackman-Harris window function [13] and zero-filled once prior to Fourier transformation. No high resolution spectra were acquired; however, with this system it is possible to obtain up to 64 k data points and apply a standard heterodyne approach [14], if necessary. In this manner we have previously obtained mass resolution ( $m/\Delta m_{\text{rel}}$ ) in excess of 40,000 [7].

## **RESULTS AND DISCUSSION**

### **Floating Conductance Limit / No Ion Flight Tube**

In order to evaluate the effect of the new transport optics independently of the previously employed four element lens, it was necessary to establish a set of "test" voltages under which the lens would constantly operate. For this purpose, the CL plate with the 1.0 mm diameter orifice was replaced with an electrically isolated solid plate, and an inexpensive 2.0 mm diameter nichrome wire was used as a sample. With the CL plate at ground potential, a  $2.9 \times 10^{-7}$  A ion beam current was measured on the #30 stainless steel mesh (0.011" wire diameter) grid (G) which was the first element of the lens (see Figure 3 for more detail of the lens - source configuration). Next, several voltage combinations were tried until a maximum current of  $1.4 \times 10^{-9}$  amperes was measured at the CL plate; this was observed with -825 V on the grid (G), -898 V on lens 1 (L1), -684 V on lens 2 (L2), and -674 V on lens 3 (L3). This result indicated a loss of at least 200 in beam current in passing through the electrostatic lens. This loss was presumably due to incomplete focussing of ions exiting the glow discharge source at large angles, neutralization of ions on the grid wires, and collisional scattering of ions by the high pressure of argon in the lens region. Variations in GD source conditions caused the absolute ion current passing through the conductance limit to fluctuate somewhat from day to day, but the maximum current at this point never exceeded  $3 \times 10^{-9}$  A.

After the solid conductance plate was replaced with a 1.0 mm diameter orifice, the ion signal was monitored by standard FTICR detection in the analyzer cell as a function of the CL voltage. Figure 4 shows that a 2 to 5 fold increase in signal intensity was obtained as a negative bias was applied to the previously grounded CL. Ion signal profiles for the  $\text{H}_2\text{O}^+$ ,  $\text{Ar}^+$ , and  $\text{Ni}^+$  species all followed similar trends, increasing sharply until ca. -75 V dc was reached, followed by a slight decrease in signal intensity over the remaining range of applied voltage. This increase in signal intensity is believed to result from the more efficient transport of ions through the CL and not any additional source of ionization.

As support for the hypothesis that the potential on the conductance limit provided for better transfer of ions from the GD source to the analyzer cell, a series of SIMION [15] trajectory calculations were performed. The initial conditions for these calculations were such that each of 13 ions with a slightly different exit angle was accelerated with 5 eV of kinetic energy into a magnetic field gradient that varied from 95 G at the source to 20,000 G at the analyzer. Each ion trajectory began 2 mm from a -0.5 V biased cathode/negative glow. Although -1500 V was applied to the cathode, this voltage drops rapidly across the "dark region" of the discharge [8]. Langmuir probe studies have indicated that ions in the discharge have kinetic energies in the range 1-10 eV, approximately following a Maxwell-Boltzmann distribution [8]. Figure 3 illustrates the SIMION trajectories for both the CL at ground potential (A) and at -75 V (B). It is obvious from the two figures that the seven ions passing through the hole in the -75 V CL were focussed better. (Six of the original 13 ions struck the CL and did not pass farther in both cases.) Interestingly, Figure 3A also predicts that only three of the thirteen ions leaving the source should pass beyond the 0.75" long x 0.5" diameter opening in the grounded flange housing.

Previously, we calculated the detection limit for the nickel analyte in a NIST 1261a stainless steel reference material [7]. For 50 scans accumulated over a 10 - 100 a.m.u. mass range, the standard deviation of the mean [16] of 5 background determinations was 15090 counts. The  $^{60}\text{Ni}$  isotope present at 0.52% yielded an ion signal of 3.5 million counts. Therefore the detection limit, calculated by multiplying the inverse of the sensitivity (1.5 ppt/count) by 3 times the mean standard deviation of the background [17] was 70ppm [7]. With the CL at -75 V, a detection limit was again calculated for the  $^{60}\text{Ni}^+$  ion generated from the NIST 1261a reference material. For 50 scans accumulated over a 10 - 100 a.m.u. mass range, the standard deviation of the mean of 5 background determinations was 17020 counts. The  $^{60}\text{Ni}$  isotope yielded an ion signal of 15.5 million counts, which corresponds to a detection limit of ca. 15 ppm, almost a factor of five improvement over the results obtained with the grounded CL.

Even though the detection limits improved with the addition of a voltage to the conductance limit, no steps had yet been taken to overcome the effects of the fringing magnetic fields. In order to evaluate those effects, the ion beam current was measured along the injection axis under our "test" conditions for both the grounded CL (Figure 5) and the -75 V CL (Figure 6). Several results are seen when comparing the two figures. First, the signal intensity 1.0" from the CL (42" from the rear trapping plate of the analyzer cell) increased ca. 7 times in applying -75 volts to the CL; this agrees surprisingly well with the results discussed in the previous paragraph obtained from ion signals detected by FTICR methods in the analyzer cell. An improvement in current of this approximate magnitude was seen over the entire distance from the conductance limit to the analyzer cell. These results imply that the fringing magnetic fields may not be playing as large a part in reducing the GD beam intensity as in some other sources [18]. Secondly, as the ion beam was monitored closer to the analyzer cell a decrease in signal was observed; this decrease occurred over the same region in which the magnetic field was sharply

increasing, a fact that is not surprising. Finally, examining either Figure 5 or Figure 6 indicates that there was still a 2 - 3 fold loss in ion current arriving at the analyzer cell compared to that at the CL, due solely to the fringing fields of the magnet. Although this loss was not as high as first anticipated, any improvement in the number of ions transported to the cell will improve the overall sensitivity. To improve ion transport, an ion flight tube was built to carry the ions from just beyond the CL, through the magnetic field, and to the analyzer cell.

### **Floating Conductance Limit / Ion Flight Tube / Ion Decelerator**

Kofel and McMahon [12] have reported an ion flight tube design that is improved with respect to earlier electrostatic ion injection schemes [3] (which are also the basis of one commercial (Spectrospin AG) FTICR external ion injection instrument). Our initial flight tube design was simpler than that of Kofel, *et al.*, as we had no additional conductance limit (even though this did result in a higher ultimate pressure in the analyzer cell), and no transport lenses before the decelerator. In addition, the flight tube and first decelerator electrode were connected electrically in our system for convenience.

Similar to the manner in which the optimum conductance limit voltage was determined, the ion signal was monitored in the ICR cell as a function of the negative bias applied to the flight tube and decelerator. The ion signal for the  $\text{H}_2\text{O}^+$  and  $\text{Ar}^+$  species increased sharply until ca. -25 V dc. Between -25 V dc and -175 V dc, the signal rose steadily; at -175 V dc the signal intensity reached a plateau, then decreased beyond -200 V dc. In this manner, a new set of optimum "test" conditions were established; these were: -825 V on the grid (G), -898 V on lens 1 (L1), -684 V on lens 2 (L2), -674 V on lens 3 (L3), -75 V on the conductance limit (CL), and -175 V on the flight tube (FT)/decelerator (D).

Next, ion trajectories were simulated to show the effect of the flight tube/decelerator combination. Under our "test" conditions, the results shown in Figure 7A were generated. This figure illustrates how incorporation of both the flight tube and floating conductance limit served to better collimate the ion beam than use of only the floating conductance limit (cf. Figure 3B). Similarly, trajectory calculations were made at the decelerator/ICR cell interface (Figure 7B). These calculations were based on 7 ions exiting the flight tube with 180 eV of kinetic energy (the initial 5 eV of kinetic energy imparted by the discharge plus the 175 eV imparted by the flight tube). Since the decelerator is virtually in the center of the superconducting magnet, a constant magnetic field of 20,000 G was substituted for the magnetic field gradient used in Figure 3 and Figure 7A. The ions were given trajectories parallel to the injection axis, beginning 2" inside the flight tube.

Closer examination of all the data used to generate Figure 7B shows that once the ions pass through the decelerator's ring electrode and into the grounded housing, they lose all but their initial 5 eV of kinetic energy. However, even after leaving the grounded



section of the decelerator, the simulated ions still possess enough energy to overcome the +2 V trapping potential at both the front and rear plates. Experimentally, the ion beam will contain ions with a distribution of energies: some with energies too low to overcome the front trapping plate voltage, which will therefore be turned around; some with energies quite close to the trapping potentials; and some with sufficient energy to overcome the voltages on both the front and rear trapping plates and pass through the cell entirely. One additional means of trapping glow discharge ions is collisions with the relatively high levels of argon in the cell. Ion-molecule collisions occurring in the region between the trap plates reduce both the overall and the z-axis kinetic energies of the ions, and therefore increase the probability that they will be trapped.

The enhanced intensities of  $\text{H}_3\text{O}^+$  and  $\text{Ar}^+$  detected in the analyzer cell when using the flight tube and decelerator indicated that these components definitely aided the transport of an increased population of glow discharge generated ions through the fringing magnetic fields. Similar to the Faraday probe experiments reported earlier, the total ion beam current was monitored along the injection axis with our new "test" conditions. Figure 8 illustrates how a virtually constant ion beam is present from the conductance limit through the fringing magnetic field and into the ICR cell. Thus the combination of a floating conductance limit, flight tube, and decelerator increased the current of glow discharge generated ions reaching the analyzer cell by a factor of almost 20 (cf. Figure 5), with no apparent ion loss in the fringing magnetic field.

Other means of transporting ions through the fringing magnetic fields (such as the use of quadrupole rods [2]) could also be used in these GD-FTICR experiments. Because of their experimental simplicity we have concentrated exclusively on the use of simple electrostatic lenses and flight tubes in our studies. Various means of enhancing the concentrations of analyte ions in the FTICR cell by selective ejection of unwanted ions ( $\text{Ar}^+$ ,  $\text{H}_3\text{O}^+$ , and major substrate ions), in particular use of the SWIFT [19] technique, have not yet been attempted but will markedly improve the sensitivity of this method.

Although glow discharge mass spectrometry has yet to flourish in the way that spark source mass spectrometry did in the inorganic mass spectrometry community, it has begun to mature as a viable technique for elemental analysis. One of its formidable limitations, isobaric interferences, continues to be addressed through research using both high mass resolving power and collision induced dissociation of polyatomic interferences. It seems only appropriate that Fourier transform ion cyclotron resonance mass spectrometry, with its unique capabilities for providing both ultra high mass resolving power and CID, should be at the forefront of this continuing research.

## CONCLUSIONS

Addition of a floating conductance limit, a flight tube, and a decelerator just before the FTICR cell have improved the transport of ions from a glow discharge source to the ICR analyzer cell by a factor of ca. 20. Residual pressures in the cell remain somewhat high (ca.  $1 \times 10^{-7}$  Torr) due to the use of only two stages of differential pumping, and mass resolving powers are less than might be achieved with lower base pressures. Spectra with considerably higher (to  $m/\Delta m_u = 290,000$ ) mass resolving power have been obtained on a commercial instrument with additional stages of differential pumping [9]. Further improvements in both sensitivity and mass resolving power can be confidently predicted, pointing to FTICR mass spectrometry as the analysis method of choice for glow discharge generated ions.

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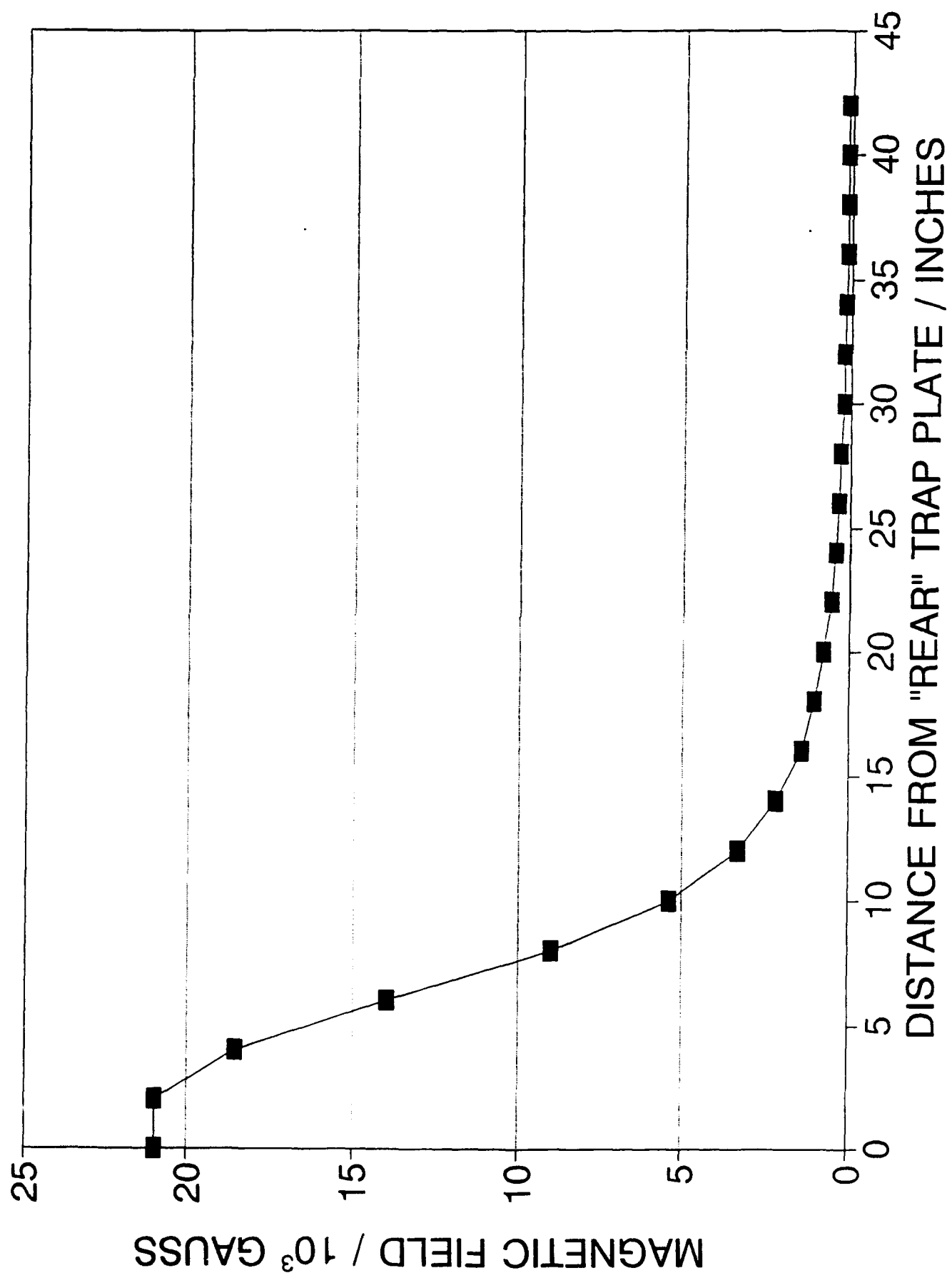
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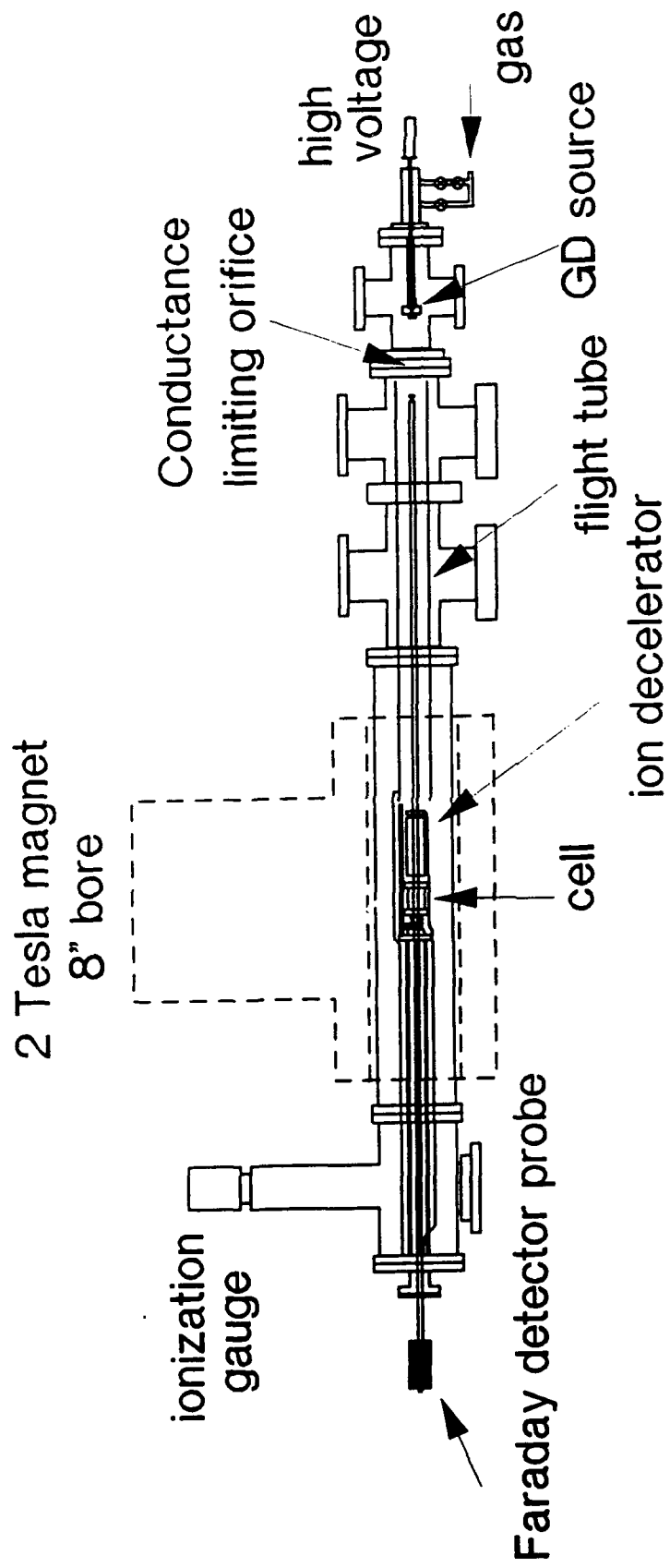
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## **FIGURE CAPTIONS**

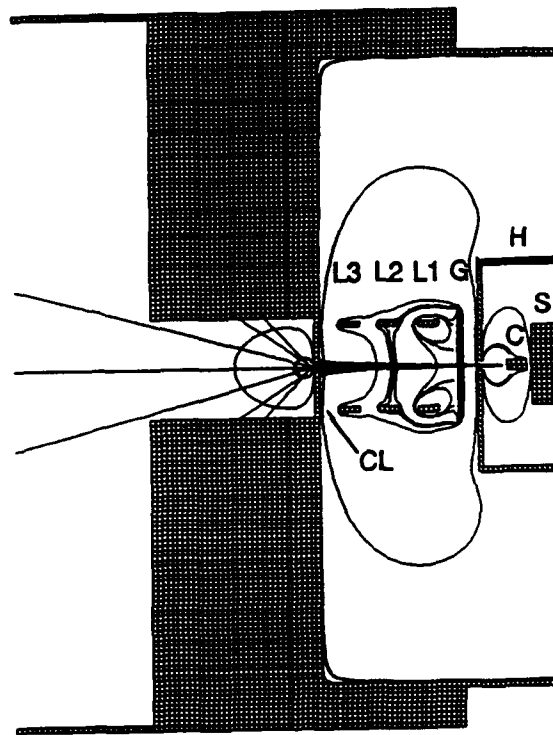
- Figure 1. Magnetic field strength versus the distance from the "rear" trap plate (see text) for the 2.0 Tesla magnet used in these studies.
- Figure 2. A glow discharge Fourier transform ion cyclotron resonance (GD-FTICR) mass spectrometer modified to accommodate an electrically isolated conductance limit, flight tube, and ion decelerator. Also shown is the Faraday cup/probe employed for total ion current detection (see text).

- Figure 3. (A) SIMION trajectories calculated for thirteen ions with 5 eV kinetic energy under the following conditions: housing (H) ground; source (S) ground; cathode (C) -0.5 V; grid (G) -825 V; element 1 (L1) -898 V; element 2 (L2) -684 V; element 3 (L3) -674 V; conductance limit (CL) ground. (B) SIMION trajectories calculated for thirteen ions with 5 eV kinetic energy under the following conditions: housing (H) ground; source (S) ground; cathode (C) -0.5 V; grid (G) -825 V; element 1 (L1) -898 V; element 2 (L2) -684 V; element 3 (L3) -674 V; conductance limit (CL) -75 V.
- Figure 4. Relative signals for water, argon, and nickel ions versus conductance limit voltage. Other lens element voltages were: grid -825 V; element 1 -898 V; element 2 -684 V; element 3 -674 V.
- Figure 5. Magnetic field strength and Faraday probe current versus the distance from the rear trap plate. Lens voltages for these experiments were: grid -825 V; element 1 -898 V; element 2 -684 V; element 3 -674 V; conductance limit ground; flight tube ground.
- Figure 6. Magnetic field strength and Faraday probe current versus the distance from the rear trap plate. Lens voltages for these experiments were: grid -825 V; element 1 -898 V; element 2 -684 V; element 3 -674 V; conductance limit -75 V; flight tube ground.
- Figure 7. (A) SIMION trajectories calculated for thirteen ions with 5 eV kinetic energy under the following conditions: housing (H) ground; source (S) ground; cathode (C) -0.5 V; grid (G) -825 V; element 1 (L1) -898 V; element 2 (L2) -684 V; element 3 (L3) -674 V; conductance limit (CL) -75 V; flight tube (FT) -175 V. (B) SIMION trajectories calculated for seven ions with 180 eV kinetic energy under the following conditions: flight tube (FT) -175 V; decelerator high voltage (D-HV) -175 V; decelerator ground (D-G) ground; excite/receive (E/R) ground; trap (T) +2 V.
- Figure 8. Magnetic field strength and Faraday probe current versus the distance from the rear trap plate. Lens voltages for these experiments were: grid -825 V; element 1 -898 V; element 2 -684 V; element 3 -674 V; conductance limit -75 V; flight tube -175 V.

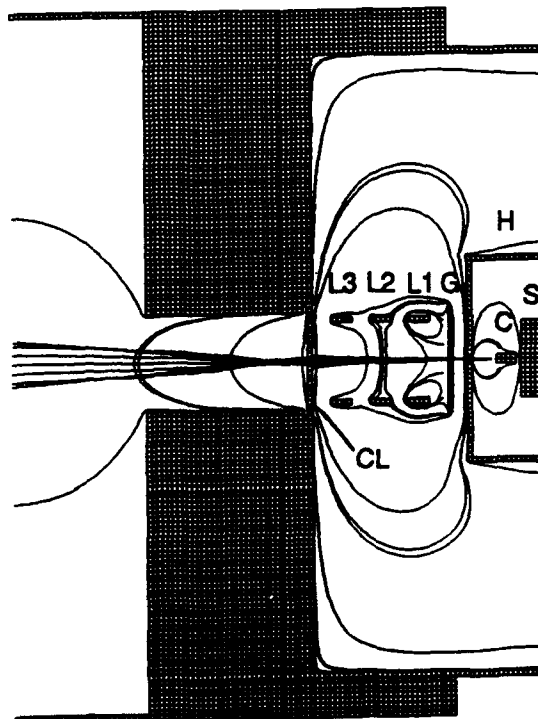


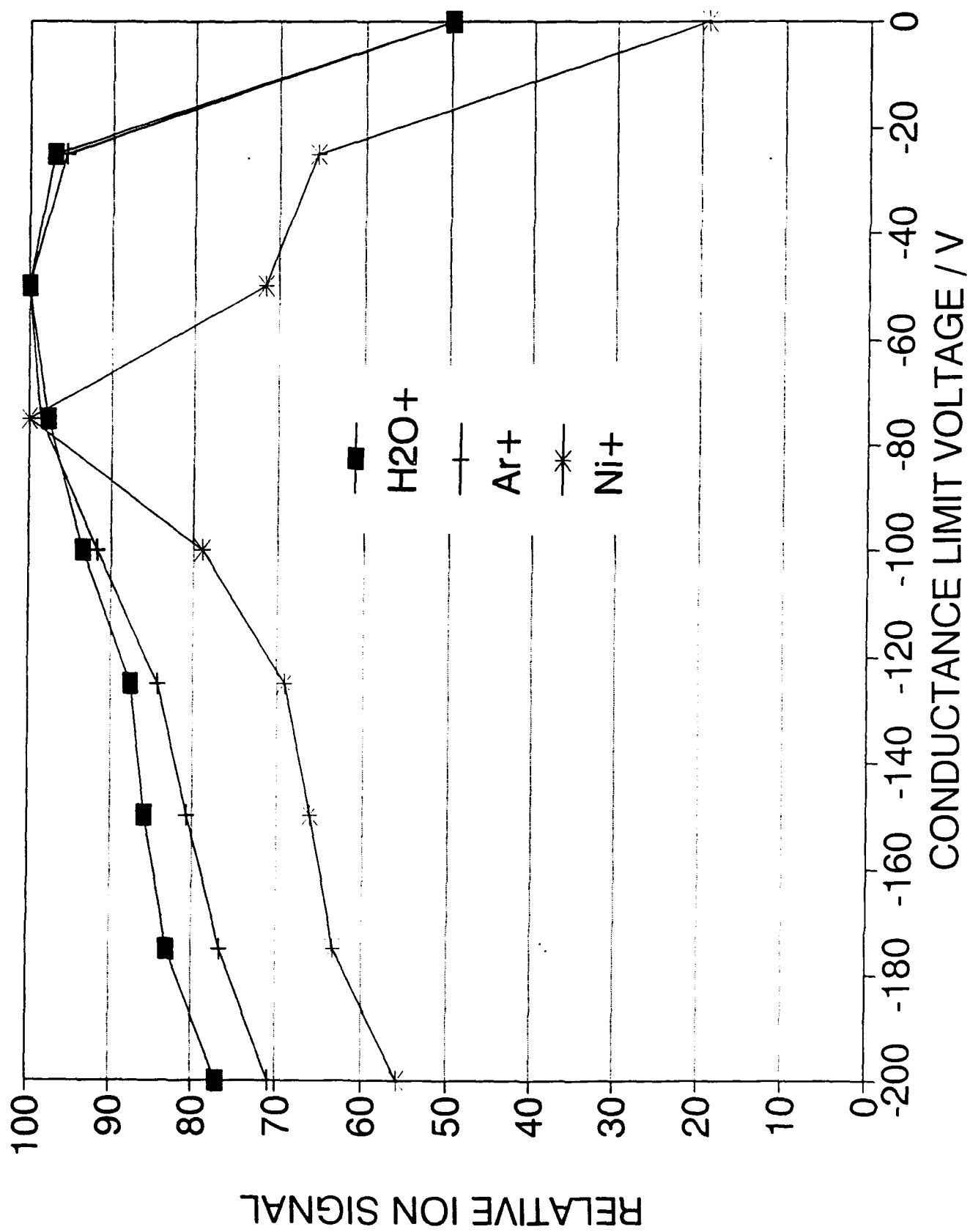


(A)

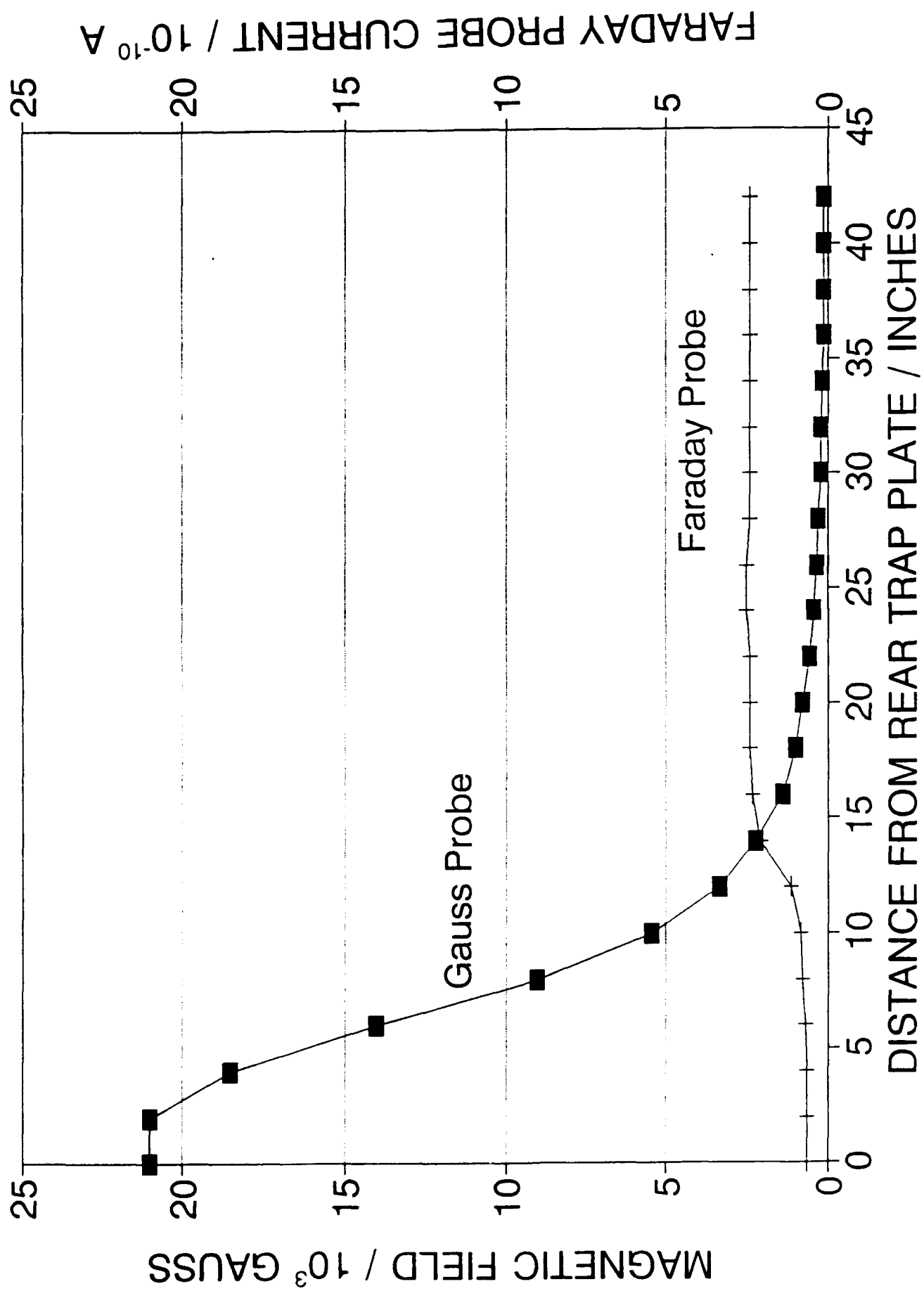


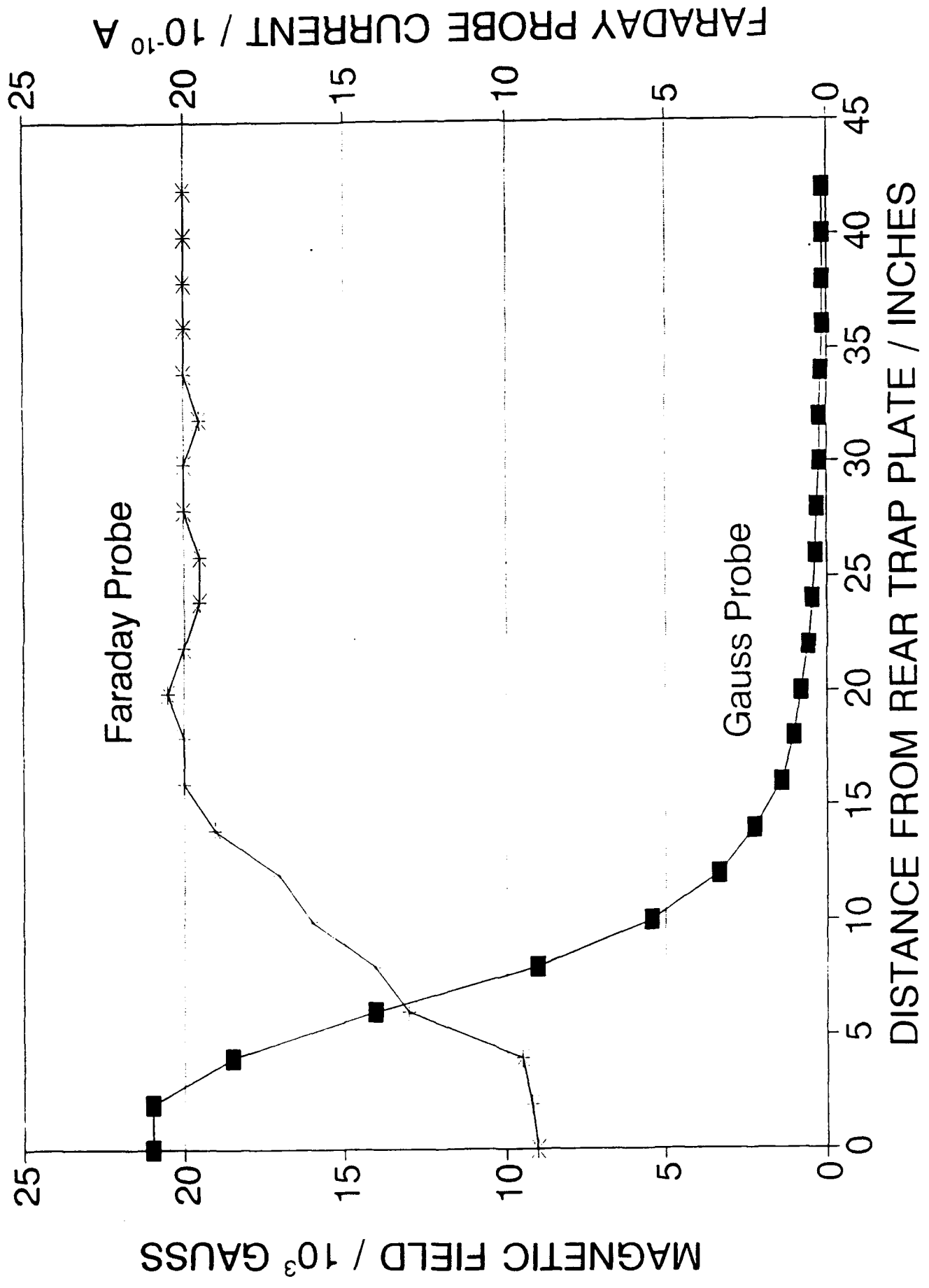
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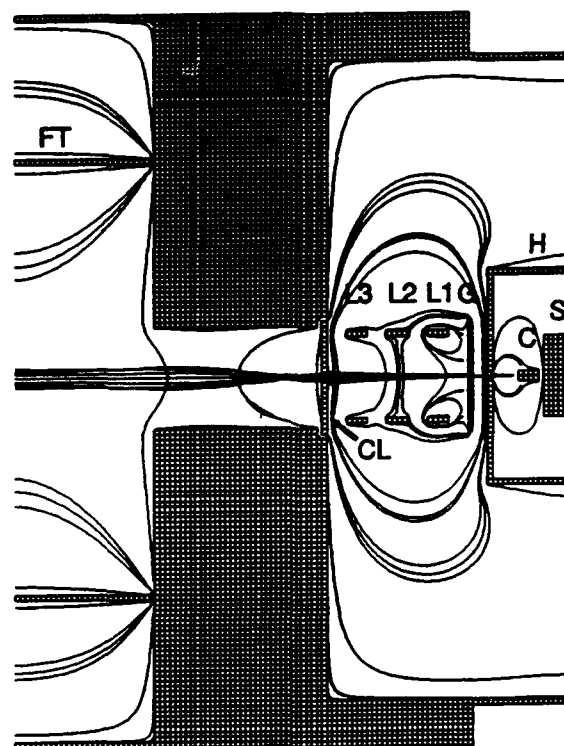








(A)



(B)

